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Self-Organized Liquid Phase and Co-Crystallization of Rod-Like Polymers Hydrogen-Bonded to Amphiphilic Molecules**

By Olli Ikkala,* Matti Knaapila, Janne Ruokolainen, Mika Torkkeli, Ritva Serimaa, Kaija Jokela, Lockhart Horsburgh, Andrew Monkman, and Gerrit ten Brinke*

The process of self-organization^[1] facilitates formation of ordered polymeric nanoscale structures,^[2–7] and hierarchical (tandem) self-organization^[8–10] further allows elaboration of responsive materials based on sequences of order-order and order-disorder transitions.^[8] Application to rod-like polymers (such as π -conjugated electroactive polymers) could lead to possible new applications, but is not straightforward because such polymers tend to be infusible and poorly soluble. For polymers containing rod-like moieties, self-organization has been achieved based on di-block copolymers with flexible blocks,^[11,12] comb-block copolymers with flexible side chains (so-called “hairy rods”),^[13–15] and sufficiently dilute mixtures with strong amphiphilic acids.^[16,17] Here we show that one of the simplest π -conjugated electroactive rod-like polymers poly(2,5-pyridine diyl) (PPY), i.e. polypyridine or poly(*p*-pyridine), stoichiometrically protonated by the simplest sulfonic acid, i.e., methane sulfonic acid (MSA), to form a polymeric salt poly(2,5-pyridine diyl) methane sulfonate, PPY(MSA)_{1.0}, forms self-organized nanoscale structures upon complexing with selected alkylphenols, such as octyl gallate (octyl 3,4,5-trihydroxybenzoate, OG). In this case, the strength of the hydrogen bonding was sufficient to compensate for the repulsion due to the alkyl tails, which is necessary for self-organization. A supramolecular structure was formed which resembled “hairy rod” polymers with a fascinating phase behavior. For example, at high temperatures, the mixture consisting of PPY (MSA)_{1.0} and OG in the molar ratio 1.0:2.0, formed a homogeneous solution at the resolution of optical microscopes. Cooling below the order-disorder tran-

sition ($T_{\text{ODT}} \approx 180^\circ\text{C}$) the mixture became a self-organized complex fluid. At still lower temperatures ($T < 110^\circ\text{C}$), co-crystallization within the polar layers, consisting of protonated PPY-chains, methylsulfonate counter ions, and the aromatic part of OG, was observed. Such supramolecular “hairy rod” complexes open a straightforward route to prepare processible (fusible) block copolymer-like ordered structures in a number of rod-like polymers.

Polymers containing main chain pyridine groups have aroused considerable interest in relation to photonic applications.^[18–26] In particular, PPY (i.e., $-(\text{C}_5\text{H}_3\text{N})_n-$) is a rod-like π -conjugated polymer^[18,19] due to its rigid para-coupled aromatic units (see Fig. 1). It is not fusible and dissolves in acidic solvents such as sulfuric acid, formic acid and dichloroacetic acid.^[19,22] Such solutions allow processing by spin casting of thin PPY films on substrates to prepare photonic devices, for example.

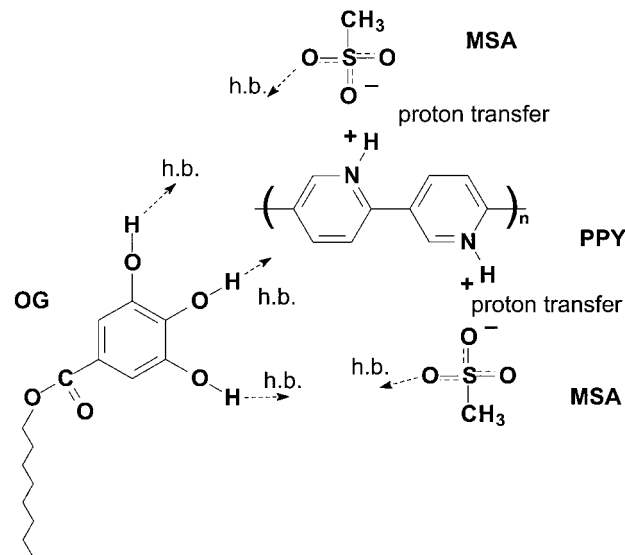


Fig. 1. Poly(2,5-pyridine diyl) (PPY), methane sulfonic acid (MSA), octyl gallate (OG), and the possible schemes for their interaction. The sulfonates of PPY(MSA)_{1.0} act as “primary” hydrogen bonding acceptors to hydrogen-bond OG, using the three OH-groups (hydrogen bonding donors). Possible primary hydrogen bonding sites have been denoted using “h.b.” “Secondary” hydrogen bonding can take place to the primarily hydrogen-bonded OG molecules using the hydrogen-bonding acceptor groups $>\text{C}=\text{O}$ and $-\text{O}-$ of OG.

[*] Prof. O. Ikkala, M. Knaapila, J. Ruokolainen
Department of Engineering Physics and Mathematics
Helsinki University of Technology
P.O. Box 2200, FIN-02015 HUT, Espoo (Finland)

M. Torkkeli, Dr. R. Serimaa, K. Jokela
Department of Physics
University of Helsinki
P.O. Box 9, FIN-00014 Helsinki (Finland)

Dr. L. Horsburgh, Dr. A. P. Monkman
Department of Physics, University of Durham
Durham DH1 3LE (UK)

Prof. G. ten Brinke
Department of Polymer Science and Materials Science Center
University of Groningen
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)

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In this paper, we adopt a different perspective to investigate whether PPY allows a prototype for conducting supramolecular self-organized assemblies and whether the properties could be externally controlled, most simply by temperature, to achieve responsive materials. The pyridyl rings are deficient of π -electrons and therefore *p*-doping yields moderate conductivity of ≈ 0.1 S/cm whereas *p*-doping, based on electron withdrawal, is ineffective^[18,19] which is also expected for protonation of PPY by strong acids. However, protonation would allow model compounds that are conceptually interesting for several reasons: a) the photophysical properties can be modified upon protonation;^[24] b) in the emeraldine base form of polyaniline (PANI), which is another nitrogen-containing π -conjugated

polymer, protonation is the commonly used p-doping to achieve conductivity;^[27] and c) emeraldine base is a copolymer of benzene diamine and quinone diimine moieties, and therefore it is more complicated to understand the formation of its complexes than in PPY which is a homopolymer. Therefore the supramolecular concepts demonstrated using PPY could also be instructive in guiding the work for PANI, in addition to the general interest for designing nanostructured electroactive rod-containing materials.

In this work, we used MSA to protonate the pyridine nitrogens of PPY (see Fig. 1). A stoichiometric complex, consisting of 1 mol of PPY repeat units vs. 1 mol of MSA, was prepared in formic acid solution, followed by evaporation of the solvent and drying. FTIR methods were employed to verify that protonation by MSA took place. The resulting polymeric salt [subsequently denoted as PPY(MSA)_{1.0} based on the nominal composition] was infusible. Figure 2 presents the wide angle X-ray scattering (WAXS) patterns. Pure PPY shows a crystalline reflection at a scattering vector magnitude $q = 1.80 \text{ \AA}^{-1}$ corresponding to the order of 3.50 \AA due to the interchain distances. In addition, another reflection at $q = 3.09 \text{ \AA}^{-1}$ (not shown in the q -range of Fig. 2) was observed due to a structure along the direction of the chains (c -direction). The crystallite size was $\approx 40 \text{ \AA}$ based on the width of the peaks. The diffraction pattern of PPY(MSA)_{1.0} differs from that of pure PPY indicating that a new co-crystallized structure has formed. This also supports the formation of a complex between PPY and MSA, in agreement with related studies using polyparaphenylene and AsF₅.^[28] The new reflections of PPY(MSA)_{1.0}, not observed in the pristine PPY, may be due to ordering of the methylsulfonate anions. The WAXS peaks were sharper which indicates that the crystallites had a larger size of $\approx 120 \text{ \AA}$. The current/voltage relationship of PPY (MSA)_{1.0} was linear at room temperature in a four-probe electrical direct current (DC) conductivity measurement, which was not expected for purely ionic conductors and suggesting

that there may be some electronic conductivity component included. Not surprisingly,^[18] the actual conductivity levels were small (of the order 10^{-6} S/cm) at room temperature. Note that even if the conductivity level is relatively low and that the actual conduction mechanism remains slightly open, we were able to establish relationships between the self-organized structures, the phase transitions, and the conductivity behavior.

To form self-organized structures, one could next covalently bond repulsive alkyl tails to PPY(MSA)_{1.0} to form comb-block copolymers, i.e., “hairy rods”.^[13–15] This scheme corresponds to “permanently” bonded alkyl solvent molecules, with their (ideally) infinite attraction to the polymer backbone. In PANI it was observed that if the strong acids capable of protonation were selected to be amphiphilic, such as dodecyl benzene sulfonic acid (DBSA),^[16] self-organization as a lamellar fluid phase could be achieved, given that excessive amounts (i.e., more than the stoichiometric amount) of DBSA were used.^[17,29] The then highly acidic groups led to a strong ionic attraction to the basic polymer backbone, thus preventing macrophase separation of the amphiphiles, which would otherwise have taken place due to the low mixing entropy and the repulsive alkyl tail. Similarly, in the case of PPY, the complexes with DBSA yielded mesomorphic structures with the long period of 27 \AA .^[30] In this case, the side groups could be regarded as being permanently bonded due to the strong proton transfer attraction between PPY and DBSA. However, as in the flexible pyridine-containing polymers, e.g., polyvinylpyridines, it was expected that even for PPY, hydrogen bonded amphiphiles offer exciting possibilities to tailor the phase behavior and functionality due to the reversibility of the attraction.^[8]

Phenols serve as model compounds for hydrogen bonding solvents. PPY(MSA)_{1.0} was observed to be soluble in *m*-cresol ($3\text{-H}_3\text{C-C}_6\text{H}_4\text{OH}$) based on an attraction due to a hydrogen bond between its aromatic hydroxyl group and methane sulfonate groups of PPY(MSA)_{1.0}. To achieve self-organization, an additional repulsive interaction was required which could be achieved by adding an alkyl tail to the phenolic group. Such a concept, however, is not straightforward because the relatively low strength of the hydrogen bond has to compensate for the repulsion. After several experiments, using phenols with different lengths of repulsive alkyl tails and different numbers of attractive aromatic hydroxyl groups, thus leading to different polarity, we selected OG, i.e., $n\text{-C}_m\text{H}_{2m+1}\text{-OOC-C}_6\text{H}_2\text{-3,4,5-(OH)}_3$ with $m = 8$). Its three aromatic hydroxyl groups and an ester group led to a relatively high polarity, allowing dissolution in formic acid, thus facilitating straightforward preparation of complexes with PPY(MSA)_{1.0}. Note that OG showed a desirable balance between the attraction and repulsion to PPY(MSA)_{1.0}. A gallate with a slightly longer tail ($m = 12$), i.e., lauryl gallate, is soluble in formic acid only under mild heating and X-ray scattering indicates that, after evaporation of formic acid, lauryl gallate macrophase separates from PPY(MSA)_{1.0}.

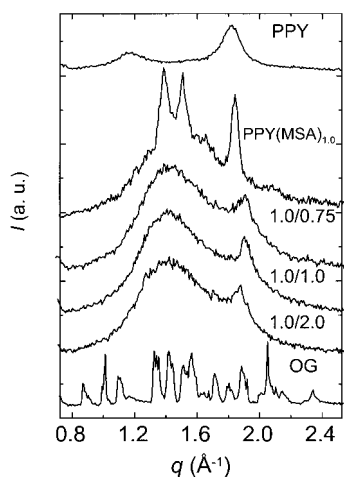


Fig. 2. WAXS patterns of PPY, PPY(MSA)_{1.0}, OG, and the mixtures of PPY(MSA)_{1.0} with OG in the molar ratios 1.0:0.75, 1.0:1.0, and 1.0:2.0 at room temperature. Note that MSA is a disordered liquid at room temperature.

Mixtures of PPY(MSA)_{1.0}/OG in the molar ratios 1.0:0.5, 1.0:0.75, 1.0:1.0 and 1.0:2.0 were prepared in formic acid solution, followed by the evaporation of formic acid and drying. In the following, PPY(MSA)_{1.0}/OG specifically with 1.0:2.0 mol/mol will be described in some detail to demonstrate the phase behavior.

Above $\approx 180^\circ\text{C}$ the sample PPY(MSA)_{1.0}/OG 1.0:2.0 mol/mol is a homogeneous fluid at the resolution of an optical microscope which suggests that 24 wt.-% PPY(MSA)_{1.0} dissolves in OG at such temperatures. This is a remarkably high solubility, given the rigid rod-like structure of PPY. The sample was not birefringent under crossed polarizers in optical microscopy, suggesting an isotropic solution rather than a nematic solution. The classical treatment of rigid rods in solvents^[31] suggests that the aspect ratio for the rods should be quite small, at most ca. $L/D \leq 10$ to achieve isotropic solution for such high concentration. In our case the estimated MW = 6000 daltons for PPY^[24,25] and the estimated diameter $D \sim 16 \text{ \AA}$ of PPY(MSA)_{1.0}, leading to $L/D \approx 16$. Therefore we could have expected nematic solutions at the current levels of concentration. Increasing the concentration of PPY(MSA)_{1.0} in OG (such as 1.0:0.75 mol/mol) yielded a two-phase structure with birefringent liquid droplets in an isotropic background liquid, suggesting that lyotropic solutions will ultimately be achieved at higher concentrations, as could be expected. The deviations from the simple model may be due to the charged PPY(MSA)_{1.0} chains or potentially the chains may actually adopt some bending.

Between 110 and 180°C the sample was a birefringent liquid in optical microscopy, indicative of optical anisotropy. To study the structure, small angle X-ray scattering measurements (SAXS) were made as a function of temperature. In the isotropic liquid state at $T > 180^\circ\text{C}$, there is only a shallow and broad SAXS peak (see Fig. 3), ascribed to a correlation hole peak.^[32,33] Cooling beyond 180°C renders a distinct SAXS peak observed at $q = 0.19 \text{ \AA}^{-1}$ which corresponds to a long period of 32 \AA . At the transition 180°C the half-width at half maximum (hwhm) of the scattering peak undergoes a step-like decrease. In addition, differential scanning calorimetry (DSC) measurements revealed that

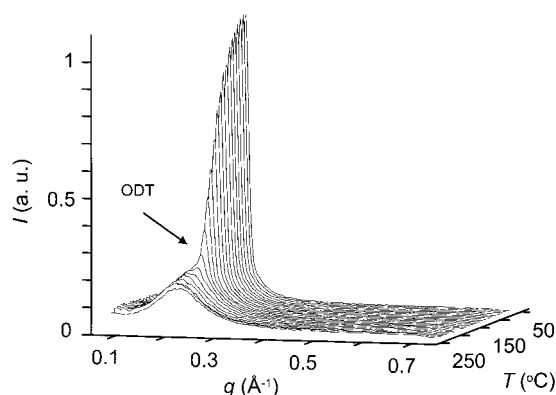


Fig. 3. SAXS patterns of PPY(MSA)_{1.0}/OG in the molar ratio 1.0:2.0 as a function of temperature during a slow cooling at a rate of 10 K/h. An order-disorder transition from isotropic fluid to mesomorphic fluid is observed at 180°C .

an exothermic peak at 180°C was observed during cooling at a sweep rate of $5^\circ\text{C}/\text{min}$. Also noting that in polarized optical microscopy, the sample became a birefringent liquid, allowed us to assign the transition at 180°C to be an order-disorder transition (ODT) in analogy with block copolymers^[2] and complexes of flexible polymers with amphiphiles.^[6,34] No higher order peaks were resolved. To see whether higher order peaks could become observable in a prolonged measurement, the temperature was next fixed at 130°C and a SAXS measurement was performed isothermally for 72 h. At the resolution of our device, no clear higher order peaks could be resolved even by the end of this period. This is not surprising, as the higher order peaks are frequently very small in the corresponding systems of flexible polymers,^[8,35] requiring higher intensity synchrotron radiation to observe them. If one assumes that all the OG molecules are hydrogen-bonded to the PPY(MSA)_{1.0} either due to primary or secondary hydrogen bonds (see Fig. 1), the combined weight fraction of the polar moieties (consisting of PPY(MSA)_{1.0} and the aromatic parts of OG) vs. the nonpolar part (consisting of the octyl chains of OG) equals the value $f = 0.69$. Although a cylindrical structure cannot be excluded based on this high value, we still suggest a lamellar structure because in widely different “hairy rods”, lamellar structures are observed for side chains of corresponding lengths.^[13,15,36] In addition, lamellar order also agrees with the observed long period 32 \AA , and the second order diffraction peak could be absent due to symmetry. Figure 4 presents the schematic structure proposed.

At 110°C a further transition took place, as demonstrated by WAXS and thermal analysis. Figure 2 shows for PPY(MSA)_{1.0}/OG with 1.0:2.0 mol/mol that at room temperature, WAXS peaks are present which were not observed in the pristine materials. Taking into account the short length of the octyl chains, this suggests that a co-crystallization took place within the layers comprising PPY(MSA)_{1.0} and the aromatic parts of OG (see Fig. 4). In addition, related WAXS patterns (although different in detail) were obtained even without alkyl tails, i.e., for mixtures of PPY(MSA)_{1.0} with resorcinol.^[37] Such structures, where one polymer and two oligomers co-crystallize, are rare, requiring molecularly matching molecules. Figure 5 shows that the co-crystalline structure melted at 110°C , as manifested also in DSC as an exothermic peak upon cooling.

Finally, DC electrical conductivity measurements were performed (Fig. 6) using a four-probe technique applying different constant currents of both polarities until the measured voltage stabilized. The stabilization was typically measured for 30 min. I - V plots were made in order to verify the ohmic nature. At temperatures $T < 110^\circ\text{C}$, where the co-crystallization within the polar layers was observed, practically no current passed and the system was highly non-ohmic. For $T > 110^\circ\text{C}$ the behavior became quite ohmic as is shown in the inset of Figure 6. The conductivity rose with increasing temperature until at 190°C the conductivity was $\sigma \approx 3 \times 10^{-5} \text{ S/cm}$. The behavior was reversible

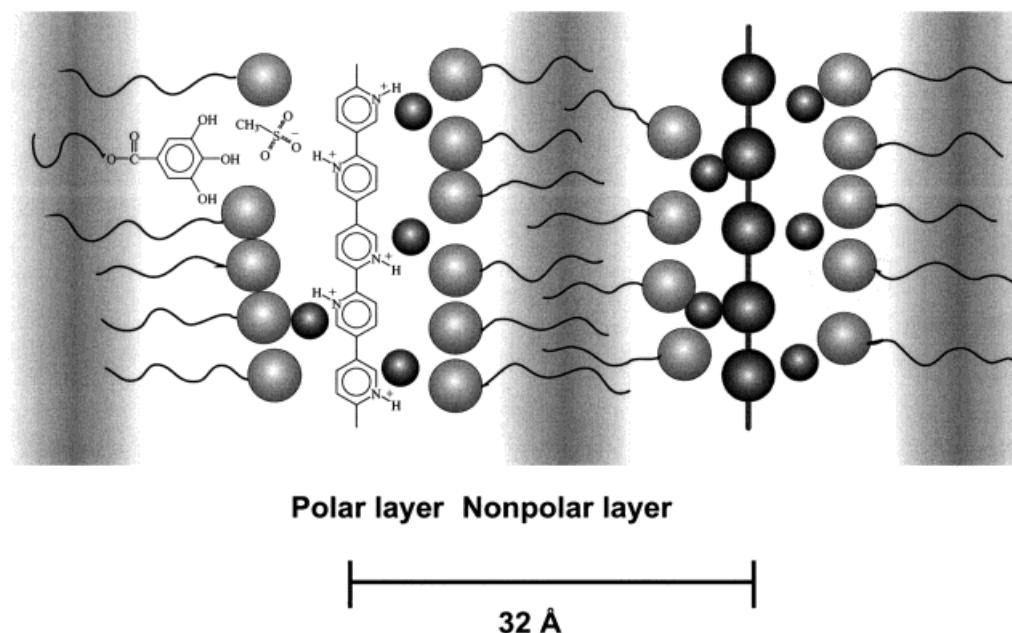


Fig. 4. Schematics of the proposed lamellar structure consisting of alternating polar layers (consisting of PPY(MSA)_{1.0} and the aromatic parts of OG) and nonpolar layers (consisting of the octyl chains of OG). The former layers adopt disordered internal structure in the mesomorphic fluid state at 110–180 °C whereas below 110 °C PPY(MSA)_{1.0} and the aromatic parts of OG co-crystallize.

upon heating and cooling. Thus one may conclude that within the present architecture, the order-disorder transition does not allow a means to control conductivity, whereas the melting of co-crystallized self-organized domains has a large reversible switching effect on the conductivity.

The results presented have many implications for new processing routes and controlled nanoscale structures of rigid rod-like polymers, and in particular, electroactive polymers. Concepts have been presented to bond alkyl chains to rigid rod-like polymers via a supramolecular route by using hydrogen bonds. Thus polymer chains have been designed with an architecture reminiscent of “hairly rods” (comb block copolymer) as a specific type of LC-coil or rod-coil polymers. Due to their block copolymer-like properties, such materials self-organize to form nanoscale structures. Therefore the phase diagram may become more

complicated than the classical phase diagram of rods dissolved in solvent, which shows only the isotropic, nematic and phase separated phases. We expect that the present concepts will open new technologically feasible possibilities to achieve controllable materials based on rod-like polymers.

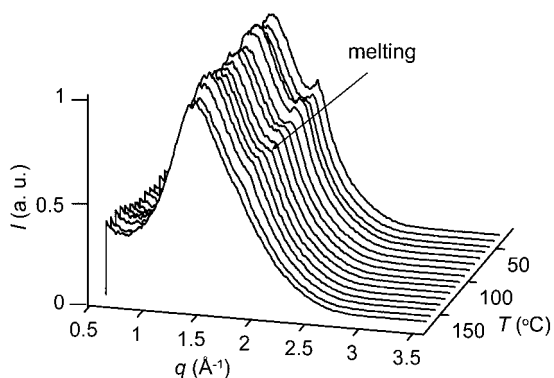


Fig. 5. WAXS patterns of PPY(MSA)_{1.0}/OG in the molar ratio 1.0:2.0 as a function of temperature during a slow heating rate of 1 K/min. The melting of the co-crystallized structures within the polar layers is observed approximately at 110 °C. The behavior is reversible upon cooling.

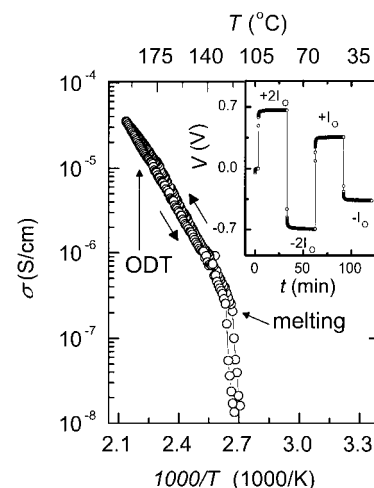


Fig. 6. Electrical conductivity of the mixtures of PPY(MSA)_{1.0} with OG in the molar ratio 1.0:2.0 during heating and cooling. The insert presents the measured voltage values as a function of time for the imposed currents ($I_0 = 50$ nA) at $T = 130$ °C, demonstrating linear current/voltage behavior. Below 110 °C the current/voltage behavior becomes non-ohmic and poorly defined, and the current transport is strongly reduced. Note that pure PPY(MSA)_{1.0} shows predominantly ohmic conductivity of ca. 10^{-6} S/cm even at room temperature and increases upon heating to 130 °C. However, the conductivity of PPY(MSA)_{1.0} is not reversible upon heating/cooling cycles, potentially due to formation of cracks in the crystalline (brittle) material caused by thermal stresses. By contrast, σ of PPY(MSA)_{1.0}/OG is reversible in consecutive heating/cooling cycles, potentially due to plasticization effect of OG to yield reduced brittleness.

Experimental

PPY was polymerized using 2,5-dibromopyridine and Ni-catalyst [24]. The molecular weight, measured by GPC and light scattering [25], is $M_n = 6000$ Da and PPY consisted of random mixture of head-to-head and head-to-tail pyridine units. Methane sulfonic acid (purity 99 %, Fluka Chemicals) was stored in inert atmosphere. Formic acid (98 %) was acquired from Riedel-de-Haën. Octyl gallate was of purity 99 % (Fluka Chemicals). It is a crystalline material with a melting temperature of $\approx 102^\circ\text{C}$.

Stoichiometric complex $\text{PPY}(\text{MSA})_{1.0}$ was prepared by dissolving equal numbers of moles of MSA and repeat units of PPY in formic acid as a 1 % solution at room temperature; after mixing, the solvent was evaporated. The complexes were dried under vacuum at 60°C for 2 days and stored in a desiccator. The changes of the characteristic FTIR peaks for $\text{PPY}(\text{MSA})_{1.0}$ compared with the superposition of those of PPY and MSA can be used to judge that the protonation takes place. Complexes with OG were made similarly in dilute solutions of formic acid, followed by vacuum drying and storing in a desiccator.

Conductivity was measured using a Keithley 2400 and a four-probe constant current method. The sample geometry was a thin film on a glass plate with gold electrodes evaporated onto the plate. The sample was sealed using another glass plate glued using epoxy. The temperature sweeps were provided by Linkham hot stage. The SAXS instrument is described elsewhere [34]. WAXS experiments at room temperature (Fig. 2) were made with transmission mode by using $\text{Cu K}\alpha$ radiation monochromatized with a quartz monochromator in the incident beam. A scintillation counter was used as a detector. WAXS experiments at elevated temperatures (Fig. 5) were performed with the SAXS setup [34] with one-dimensional position sensitive detector. The distance between the sample and the detector was 4.5 cm and the angle between the detector wire and the primary beam was 20° .

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Molecular Engineering of Push-Pull Phenylpolyenes for Nonlinear Optics: Improved Solubility, Stability, and Nonlinearities**

By Valérie Alain, Laurent Thouin,
Mireille Blanchard-Desce,* Ulrich Gubler,
Christian Bosshard, Peter Günter, Jacques Muller,
Alain Fort, and Marguerite Barzoukas

Over the past few decades, there has been considerable interest in the study of the nonlinear optical (NLO) properties of organic materials due to potential applications in various fields, such as telecommunications, optical data storage, and optical information processing. The design of NLO chromophores exhibiting enhanced molecular quadratic (or cubic) responses is a requisite for the design of efficient second-order (or third-order) NLO materials.^[1–3] In particular, much effort has been concentrated on the optimization of the typical “push-pull” structure, i.e., of molecules that bear an electron-donating group and an electron-withdrawing group interacting via a π -conjugated system.^[4] Recent studies have

[*] Dr. M. Blanchard-Desce, Dr. V. Alain, Dr. L. Thouin
Département de Chimie, Ecole Normale Supérieure (UMR 8640)
24 rue Lhomond, F-75231 Paris Cedex 05 (France)
U. Gubler, Dr. C. Bosshard, Prof. P. Günter
Nonlinear Optics Laboratory, Institute of Quantum Electronics
ETH Hönggerberg, CH-8093 Zürich (Switzerland)
Dr. J. Muller, Dr. A. Fort, Prof. M. Barzoukas
Institut de Physique et Chimie des Matériaux de Strasbourg (UMR 7504)
23 rue du Loess, F-67037 Strasbourg Cedex, (France)

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